Achieving Zero Liquid Discharge in the Semiconductor Industry

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Executive Summary

This report is an investigation into the implementation of water conservation techniques in the electronics industry. The electronics industry was chosen as a point of interest because of the ubiquity of its products, their importance as well as the relative ease for technological improvement in its methods. The electronics industry is dynamic and cutting edge. With fabrication plants turning over methods and processes at maximum every five years, the potential exists for continual improvement in efficiencies and waste reductions.

Electronics have contributed significantly to the advancement and improvement of life around the world. However, the manufacturing of silicon wafers is a very resource intensive process. It requires ultra-clean conditions and large inputs of energy, water and capital. The manufacturing process is also very complex involving several hundred steps including wafer preparation, oxide film growth, photolithography and circuit patterning, acid etches and ion deposition. Between chemical steps, ultrapure water (UPW) is always used to remove any unwanted residues from the wafer surface. This can add up to as much as 2000 gallons of water for one 8” silicon wafer (Pacific 1999). In the face of an impending global water crisis as identified by the United Nations, the need exists for water conservation methods as an every day part of life. Thus it is important to find ways to sustain the industry in the years to come that will not put excessive weight on our natural resources.

The purpose of this investigation is to assess if zero liquid discharge (ZLD) can be achieved as a solution for water conservation in the semiconductor industry. For the purpose of this investigation, ZLD is defined as the total elimination of liquid waste discharge from a plant. In place of disposal, internal waste could be recycled, reused or reduced to achieve zero output of liquid waste.

While some researchers and industries support the concept of ZLD, there are also some who are skeptical about its potential. There are some industries that would claim that they have already achieved zero liquid waste output from their plants, while still others would balk at the suggestion. Based on published information, conclusions are difficult to draw. However, for the purposes of my project, I analyzed the advantages and disadvantages of ZLD based on economics as well as on engineering feasibility. I also looked at a case study where ZLD was attempted and identified where it either succeeded or failed for that company.

Zero liquid discharge was found to be economically advantageous based on cost analysis data(Krishnan). The ability of industry to engineer an effective and sustainable process was however much more difficult to prove. In order to achieve zero liquid discharge, the concept of recycle, reuse and reduce must be implemented and achieved. Many designs have been put forward and I present a simplified model within my paper that is often used in industry.

In the practical application of these models, water conservation rates are high and financial savings are huge but technology has not yet reached the stage where total liquid discharge can be economically eliminated from semiconductor industry. The energy input required to eliminate total liquid discharge far exceeds the cost of disposal and for an industrial business interested in bottom line returns, this may not be the best option for their sustainability. However, ZLD should be used as a goal in the semiconductor industry and all water conservation efforts geared toward that end.
Introduction

In the past hundred years, technology has drastically improved the quality of human life in most parts of the world. However, by the same token, it has also increased our demand on natural resources as well as multiplied the amount of waste that is produced. One such industry is the electronics industry, in particular the semiconductor manufacturing industry. The birth of the semiconductor has revolutionized the way in which we live. Their impact ranges from research on the human genome project to the brewing of your morning cup of coffee. Semiconductors are also used in consumer electronics, telecommunications equipment and transportation equipment. In fact, any product that uses electricity and can be programmed or told what to do uses semiconductors. Although semiconductors have allowed for great advances in many diverse areas, they are not without costs.

The Semiconductor Manufacturing Process

The manufacturing process, illustrated in Fig. 1 requires ultraclean conditions and is very resource intensive. First, raw silicon wafers are prepared by the cutting and polishing of pure silicon ingots. Next a layer of oxide is deposited on top of silicon wafer in a thin film and this oxide is covered with a photoresist substrate. Patterns are imprinted through masks on this material using UV light that denatures the substrate and makes it soluble in water. The wafer is washed away with UPW, exposing the oxide layer underneath which is then etched using acids that leave bare silicon metal exposed. The silicon is then doped with ions to alter its chemical properties. These last four steps can be repeated as many as twenty times before one circuit is complete and one wafer can have anywhere from 200-300 integrated circuits. UPW is always used between chemical steps to remove any unwanted residues from wafer surface. (Intel’s website). Moreover, other processes used in wafer fabrication, including chemical mechanical polishing (CMP) which uses abrasive slurries to flatten the copper connections between circuits, also utilizes UPW to remove any residues after polishing. As a result of these stringent conditions, the manufacturing of just one 8” wafer

Figure 1: The photolithography and etching steps
can use as much as 2000 gallons of water. Two thousand gallons of water is enough to provide an entire household with enough drinking water for one month.

*The So-Called American Water Crisis?*

Is this a cause for concern? In general, the indiscriminate use of any material is to be avoided. However, the need for water conservation is one of the most pressing global issues today. Throughout the world, there is an overall shortage of water resulting from the effects of climate change as well as the rapid increase in world population. A United Nations report released on World Water Day 2002, predicted that by the year 2025, water shortages could affect two out of three people around the world. Closer to home is the fact that the last ten years have seen a mini-drought pattern in several states in the US. The largest aquifer, the Ogallala, is being depleted at a rate of 12 billion cubic meters (bcm) a year. As this map shows more than half of the nation is experiencing less than 100% of the normal precipitation received between 1971-2000. The most drastic impacts can be felt in southern states such as Arizona, New Mexico, Texas, and California.

![Map representation of drought effects in the United States](image-url)

*Figure 2. Map representation of drought effects in the United States*
Purpose of Investigation and Definition of Terms

The purpose of this investigation is to assess if zero liquid discharge (ZLD) can be achieved as a solution for water conservation in the semiconductor industry. For the purpose of this investigation, ZLD is defined as the total elimination of liquid waste discharge from a plant. In place of disposal, internal waste could be recycled, reused or reduced to achieve zero output of liquid waste.

The semiconductors industry includes establishments that manufacture semiconductors and other components for electronic applications, including capacitors, resistors, microprocessors, bare and loaded printed circuit boards, electron tubes, electronic connectors and computer modems.

Recycling is defined as the treatment and reuse of liquid waste in the same process from which it was obtained. This can be done in two ways: 1) the cleanest streams can be recycled as this reduces energy and material input into the cleaning processes or 2) all possible waste streams are recycled which maximizes the water output (Mendicino, 1999). Both options have their advantages, however for the purposes of this investigation where energy conservation was secondary to water use reduction, the recycling of all possible waste streams was chosen as the more viable scenario.

Reduction is the decrease of water input into the wafer manufacturing process which thereby also decreases the water output. Waste streams can be reduced in several ways. For one, the wafer fabrication process can be redesigned to reduce chemical use thereby reducing water needed for rinsing. In addition, control software can be used in the fab which allows for flow optimization and the elimination of autodump schedules. Instead UPW dumping should be based on contaminant levels instead of being done on a time scale. Moreover, the dilution of acids used in the etching process would also limit the amount of water required for rinsing. For the purposes of this investigation, it was assumed that industries already practice minimum water input processes.

Reuse is the treatment and use of liquid waste in another process from which it is obtained. Water that is considered too “dirty” to clean could be segregated from the other streams, treated and applied to gray water uses which include watering lawns and use in cooling towers and scrubbers. In order for water to be reused, proper segregation of liquid waste is necessary based on contamination levels. A number of gray water uses were discussed within this investigation.
Methods of Investigation

Throughout the execution of this investigation, the goals and methods have changed significantly from the starting objectives. Initially, I intended to assess the potential of a particular electronics firm in the area (namely IBM) to achieve zero liquid discharge, making use of their own specifications and parameters. However, I was unable to get in contact with someone at the company that could give me the desired information. As a result I decided to find typified data for a generic semiconductor fab and using Simo Pro Analysis 6.0, design a water recycling project that would have the least impact on the environment. This approach also created certain problems, as unfamiliarity with the software and my inability to manipulate the tools did not allow me to execute this plan effectively.

In the final output of my paper, the main method of investigation was done by extensive literature reviews of sources obtained from the Internet, published articles and electronic journals. As a result, the majority of the data is from secondary sources. Some of my information was also obtained from a phone interview with Nikhil Krishnan, a postdoctoral research fellow at Columbia University on December 5th, 2005. Through this interview I was able to obtain a better perspective on ZLD as well as a number of references. Krishnan also advised against using LCA analysis within my project as it would not provide additional information that could not be obtained from a side by side analysis of tables and charts that I had already obtained.

The data was used to compile a list of advantages and disadvantages of zero liquid discharge model based on others that I had seen in Mendicino, 1999 and DeGenova 2000. The final design was my own, though not purely original and I was able to use the literature to assess its feasibility based on economics and engineering practicality. I also investigated a case study of zero liquid discharge within the Texas Instruments factory in Dallas, TX 2000. Using these results, I was able to extrapolate the effects to the rest of the industry and estimate the practical returns and benefits that can be expected from such a system.
**Results of Investigation**

Upon researching expert opinions, the following advantages and disadvantages were obtained for and against the concept of zero liquid discharge.

<table>
<thead>
<tr>
<th><strong>Advantages</strong></th>
<th><strong>Disadvantages</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction in water/ energy demand</td>
<td>Possibility of contamination to product</td>
</tr>
<tr>
<td>Zero pollution</td>
<td>Solid/ concentrated brine effluents</td>
</tr>
<tr>
<td>Bottom line savings</td>
<td>Higher capital or retrofitting costs</td>
</tr>
<tr>
<td>Improved reliability; reduced downtime</td>
<td>Community distrust of water quality</td>
</tr>
<tr>
<td>No need to worry about EPA compliances</td>
<td>Engineering concerns</td>
</tr>
<tr>
<td>Community acceptance and trust</td>
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Table 1: Advantages and Disadvantages of Zero Liquid Discharge
The first chart shows cost analysis data which compares the cost for treatment of rinsewater and direct discharge as opposed to treatment of rinsewater and recycle through the fab.

**Comparison of Costs for Water Discharge vs. Water Recycle**

- Savings add up to over $300,000/year

Figure 3. Cost analysis results for water treatment in California (Krishnan, unpublished)
The following table compares the quality of water obtained from RO and EDI as obtained from Texas Instruments Research Study in Sandia National Laboratories, 2000.

<table>
<thead>
<tr>
<th></th>
<th>Municipal Source</th>
<th>MDL UPW</th>
<th>Spent Rinse</th>
<th>R/O Product</th>
<th>EDI Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (kohm-cm)</td>
<td>4</td>
<td>~18,000</td>
<td>2-200</td>
<td>1000-2000</td>
<td>&gt;10,000</td>
</tr>
<tr>
<td>pH</td>
<td>7-8</td>
<td>6-7</td>
<td>2-10</td>
<td>6-7</td>
<td>6-7</td>
</tr>
<tr>
<td>Dissolved Silica (ppb)</td>
<td>&gt;5000</td>
<td>2-3</td>
<td>3-30</td>
<td>500-1000</td>
<td>1-2</td>
</tr>
<tr>
<td>TOC (ppb)</td>
<td>&gt;3500</td>
<td>1-2</td>
<td>5-200</td>
<td>5-10</td>
<td>10-100</td>
</tr>
<tr>
<td>DO (ppb)</td>
<td>saturated</td>
<td>10-100</td>
<td>&gt;5500</td>
<td>50-300</td>
<td>10-30</td>
</tr>
</tbody>
</table>

Table 2. Water Quality Analysis of Municipal Source water, spent rinsewater, RO product and EDI product (DeGenova, 1996)

Chart Two shows a simplified model of zero liquid discharge that is often implemented within industry. This model was adapted from the schematic obtained in Mendicino’s case study report on water recycling in a Motorola semiconductor fab in Austin, Texas.

**Simplified Diagram of Zero Liquid Discharge Model**

![Image of simplified diagram](Image)

Figure 4. Simplified Diagram of Zero Liquid Discharge Model (Mendicino, 1999)

**Case Study: Texas Instruments, Dallas TX (DeGenova, 2000)**

Texas Instruments is one of America’s largest semiconductor providers. As an international electronics company, Texas Instruments (TI) is dedicated to the concept of
zero: zero injuries, zero illnesses, and zero waste. Thus they are an excellent study in what is currently being done in the semiconductor industry to achieve zero output liquid waste. Starting in 1995, with the implementation of its XL Project in New Mexico, TI has somehow managed to continue to reduce incoming water supplies while still boosting revenues as shown in fig. 5.

The case study under investigation in my project is the installation of a water recycling use at the manufacturing site in Dallas, TX. Installed in 1994, the treatment loop operates under the principles of:

- Re-use of reject streams and industrial wastewaters in scrubbers and cooling towers where appropriate.
- Segregate, collect, monitor, and recycle clean spent rinsewaters back to the UPW facility for re-use as Ultrapure Water.
- Use unpolished DI water for lower water quality demands.

The components of the treatment loop installed at the Dallas fab consisted of:

1) An activated carbon column – adsorbs particle contaminants from the feed
2) A large particle filter - for the removal of macroscopic material
3) A reverse osmosis membrane – removes >98% of dissolved solids, TOC and silica
4) A UV light sterilizer – used for the material of bacteria and TOC
5) Electrodionization column – uses electrochemical ideas to regenerate purified water from a solution

A more detailed description of each of these technologies is beyond the scope of this paper.

Advantages gained from the TI recycling strategy included the following.

- Annual savings of over 263 million gallons (slightly over forty percent of input) of water and a cost savings of $700,000
- Final improvement of UPW quality used on the wafer.
- Less dependence on municipal supply.
- A more reliable UPW system to our fabs, with less downtime.
- Less regenerations, less membrane cleanings, less expenditure
- Reduced chemical usage for ion exchange regenerations.
**Analysis and Discussion of Results**

As can be seen from Table 1, there is much to be said for and against zero liquid discharge. It may be difficult to draw conclusions from these opinions, as individual companies will need to weigh the costs of each option for themselves. One point of interest is the implication that zero liquid exchange can only be achieved at the expense of more solid waste being generated. However, generally speaking, more use can be found for solid waste such as chloride or copper salts than can be obtained from water perceived as “dirty”. Thus this negative is also a potential positive as solid wastes present a potential product for sale. In addition, the money saved through ZLD as well as that obtained from the sale of its byproducts will pay for the costs of retrofitting and capital that must be invested. For the purposes of this experiment, the rate of returns was not investigated, however considering the case study of TI, we can assume that it is a fairly quick process.

The economic advantage of ZLD is also apparent from Figure 10. This is not surprising as material use is directly proportional to product cost and a reduction in one will result in the reduction of the other. The data show that although treatment and recycle make use of a greater amount of capital, energy, and consumables, treatment and discharge uses more water and disposal costs. Overall, recycling uses almost 20c less per wafer pass. This represents a significant amount of savings and can add up to as much as $300,000 annually.

However, an important consideration to bear in mind is the potential for contamination to product. As interconnecting circuit lines shrink as low as 0.18 microns, even one dust particle, typically with a diameter of 0.5 microns can completely ruin a circuit. Thus, this requirement of ultraclean conditions and the engineering technologies that exist to achieve this will be the deciding factor in the further acceptance of water recycling in the semiconductor industry.

If water is to be economically conserved, it is important to assess which waste streams would be most advantageous to recycle. Table 2 shows that both water obtained through reverse osmosis and water obtained from deionization(EDI) within the UPW
generation process were several degrees above municipal source water quality. However, based on the few data points available it would appear that for recycling back into the wet tool process, the water obtained from EDI would require less energy. This differs slightly from the flow chart that I have created for the recycling process. The model was chosen due to my investigation assumptions which were that the maximum amount of water streams be recycled instead of only the cleanest streams. In addition, there is inconsistency in data sources, since the case study was done for Texas Instruments while the flowchart was obtained from Motorola data. This goes to emphasise the point that there is no one fit solution for water conservation in the electronics industry and cases must be investigated individually to assess their company’s needs.

While details may differ, the results gained from one firm can be extrapolated to estimate the effects to the rest of the semiconductor industry. As we see from the case study of TI in Dallas, TX., water conservation methods are not only possible, they also reap many benefits. In addition to annual expenditure reductions, there are other improvements in efficiency as well. As the diagram shows, constant monitoring is a must. The flow chart shows some areas where monitoring is most appropriate but these do not have to be the only points. Dirtier streams can be diluted with clean waste streams and depending on their quality, be sent directly through a water treatment process that relies on filtration, de-ionisation and reverse osmosis units. After proper treatment, these streams can also be recycled back into fab usage or used for grey water purposes such as cooling, scrubbing or watering lawns. In theory, all streams can undergo a process that enables their reuse or recycle.

However, the results obtained from the case study of TI in Dallas would lead to a different conclusion. Though in operation now for over a decade, TI still has not reduced its total water intake by more than fifty percent. Why is it that they have not achieved ZLD? Basic thermodynamic laws and material science limit the amount of water that can be economically recovered. For instance reverse osmosis can remove all dissolved materials once there is a sufficient pressure gradient across the membrane. However, large pressure gradients require large energy inputs as well as a material that will not be destroyed under high pressure. The costs involved in maintaining these conditions are much more than the cost of disposal. For a modern plant interested in maximizing revenues, the costs of water purification and recycle is not worth the returns, which is why water is often diverted to an outside treatment facility after wafer rinsing.

**Conclusions and Recommendations**

The results of this investigation lead to the conclusion that although water recycling in the semiconductor industry has been proven to be both achievable and profitable, the potential for zero liquid discharge is still unrealistic. While water recycling is achieved with high rates of water conservation and financial savings, basic thermodynamic laws and material science limit its applicability. The energy input required to eliminate total liquid discharge far exceeds the cost of disposal and for an industrial business, interested in bottom line returns, this may not be the best option for their sustainability. Until then, it is recommended that ZLD be used as an ideal situation in the semiconductor industry and all water conservation efforts be compared with its results to produce relative efficiencies.
References


- Donovan, Robert; Timon, Robert; DeBusk, Michael; Jones Ronald; Rogers, Darell. “Performance of a Treatment Loop for Recycling Spent Rinse Waters” Published by Sandia National Laboratories, Nov 15 2000

- Krishnan, Nikhil, to be published.


- Murphy, Cynthia; Laurent, Jean-Phillippe; Allen, David. "Life Cycle Inventory Development for Wafer Fabrication in Semiconductor Manufacturing" published by IEEE 2003


- "Inside the Intel Manufacturing Process: How Chips are Made" http://www.intel.com/education/makingchips/